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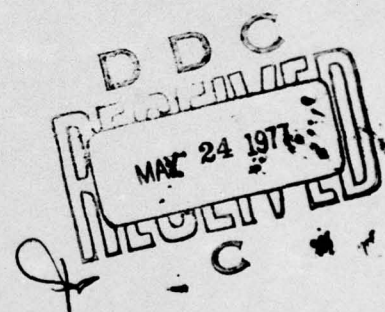
 
NRL Memorandum Report 3489

Estimation of Relative Esterification Rates by Gas Chromatography as an Aid in the Identification of Fatty Acids

PAUL J. SNIEGOSKI

*Surface Chemistry Branch
Chemistry Division*

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NAVAL RESEARCH LABORATORY
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ESTIMATION OF RELATIVE ESTERIFICATION RATES BY GAS CHROMATOGRAPHY AS AN AID IN THE IDENTIFICATION OF FATTY ACIDS

INTRODUCTION

Although the rate at which compounds react with an appropriate reagent may be a satisfactory parameter for the purpose of identification, this approach by GLC analysis is seldom used because of its inconvenience (1). This report describes a simple method utilizing GLC analysis for obtaining reliable estimates of relative esterification rates (HCl catalyzed in methanol) of unknown acids. All that is essential is a reasonably quantitative chromatographic procedure for resolving a set of acids and their methyl esters.

The procedure is a modification of a method in which the relative rates of a variety of aliphatic acids were determined by GLC methods (2). The concept of the determination is based on the equation for the relative rates of two homocompetitive reactions (3):

$$r = k_1/k_2 = \ln A/\ln B \quad (\text{Equation 1})$$

where A is the fraction of acid 1 and B the fraction of acid 2 remaining after the partial esterification. In the procedure a normal acid is added to the unknown acids. After partial esterification has taken place, appropriate GLC analysis gives the data from which the relative rate estimates of the unknown acids can be calculated. Several examples are given in the experimental section.

Note: Manuscript submitted April 8, 1977.

EXPERIMENTAL

Apparatus and Chromatographic Conditions

GLC analyses were carried out on a Beckman GC-4 gas chromatograph equipped with a flame ionization detector which was interfaced with a Perkin-Elmer PEP-1 data processor. The 6 ft x 0.125 in stainless steel column was packed with 20 percent diethyleneglycol adipate polyester and 3 percent phosphoric acid on 60/80 mesh Gas-Chrom P. The inlet temperature was 200°C and the column temperature was programmed from 60 to 180°C in 16 minutes.

Procedure

For purposes of this procedure, it is assumed that the free acids have previously been separated from other components and ether-extracted (4). An ether solution of one percent each of hexanoic, isovaleric, and 2-ethylhexanoic acids was used to demonstrate the general method. To a 5-ml portion of this sample were added 5 ml of methanol and two drops of concentrated hydrochloric acid. After standing for 35 minutes at room temperature (25° C), the mixture was analyzed by GLC. Two acid mixtures: one of heptanoic acid and 2-ethyl-3-methylbutanoic acid and the other of 2-ethyl-3-methylbutanoic acid and triethylacetic acid were utilized to further demonstrate the method where acid components with exceptionally slow esterification rates are encountered.

Results and Discussion

In the general procedure a known normal acid with a convenient retention time is added to the unknown acids. Esterification is allowed to proceed one-half to one hour. Under the conditions described in the experimental section the esterification will not exceed 85 percent so that hydrolysis effects will not be important. The ether present in the mixture will slow down the actual reaction rates but should not affect the relative rates.

Esterification data are given in Table 1. The first acid in each group is considered to be the added known acid. Calculation of the relative esterification rate, utilizing the GLC areas values, is based on the following equation:

Relative rate
of unknown acid =
at 40 C

T/313

relative rate
of known acid x

$$\left[\frac{\ln \frac{(\text{unknown acid})}{(\text{unknown acid}) + c_u (\text{unknown ester})}}{\ln \frac{(\text{known acid})}{(\text{known acid}) + c_k (\text{known ester})}} \right]$$

This equation allows relative rate values to be directly compared with the data in reference 2. The value for the relative rate of a normal acid above propionic in molecular weight is 1.00. The exponential temperature correction factor at which the esterification takes place should apply to this reaction (5). The c's are correction factors for the various acid ester pairs and can be estimated from the following:

$$c = \frac{(\text{no. of C's in the acid}) - 1}{(\text{no. of C's in the ester}) - 1} \quad (6)$$

The heptanoic acid and methyl heptanoate pair was experimentally found to give a value of 0.84 ± 0.05 over a range of acid to ester of from one-to-one to 1000-to-1. For the unknown acids, the number of carbons can be estimated from the GLC retention data; i.e., the carbon number of the next normal acid that follows the unknown acid. An error of one unit in a carbon number causes little error in the final estimated relative rate.

The calculations are illustrated from the data of the first group in Table 1 where hexanoic acid is considered the added normal acid and 2-ethylhexanoic acid the unknown.

$$\begin{aligned} \text{Relative rate of} \\ \text{2-ethylhexanoic} &= 1.00 \times \left[\frac{\ln \frac{45.38}{45.38 + (0.86) 1.11}}{\ln \frac{13.45}{13.45 + (0.83) 36.00}} \right]^{298/313} \\ &= 1.00 \times \left[\frac{\ln 0.979}{\ln 0.310} \right]^{0.952} = 0.022 \end{aligned}$$

Values determined for the two "unknowns" in the first group of Table 1 are fairly close to literature values. In the second group very little of the slow-reacting "unknown" acid has esterified giving an estimate with reduced accuracy. The procedure should give

satisfactory estimates with acids having relative rates greater than 0.001. Slower reacting acids would fall into a "slow" category by this method.

To obtain a better estimate of the rate of a "slow" acid, it is necessary to employ a slow-reacting "known" and a longer reaction time. As an illustration, 2-ethyl-3-methylbutanoic acid is used as the "known" whose rate is compared with that of the "unknown" triethylacetic acid. Even though very little of the "unknown" has reacted after 22 hours, an estimate of the relative rate can be made. Figure 1 shows the chromatogram of this esterification mixture.

Since at least 15 percent of an acid remains at the time of GLC analysis, the method is limited to a large extent by how small an amount of ester can be quantitatively measured. When only small amounts of ester are present, the tailing of the methanol becomes an important factor in the deterioration of the quantitative aspect of the method. Little esterification appears to take place in the chromatographic system. In the case of 2-ethyl-3-methylbutanoic acid in methanol-ether, the amount was found to be 0.03 percent, whether or not the catalyst was included. This would bear out the claims of Juvet and Wachi (7) that HCl is catalytically inactive in the GLC system. The GLC system described is useful for obtaining esterification data of acids in the C-4 to C-12 range. If more resolution is essential, the use of capillary columns should be investigated (8). Although the present study dealt with alkyl-substituted acetic acids, the method could be applied to other types of carboxylic acids, such as unsaturates, cyclics, and aromatics. Guides as to the effect of structural modification on the esterification rates of such acids are available (9). Where literature values are not accessible, a relative rate can be conveniently determined from a known sample with little more effort than is required for the determination of a relative retention time.

In many cases the relative esterification rate would be a helpful parameter in determining the identity of an unknown acid. The ease with which the relative esterification rate can be estimated by this method should make it a useful one.

TABLE 1

Esterification Data and Results

Acids	GLC Area		React. Temp. °C	c	Fract. Acid Remain.	Rel. Rate 40°C	
	Acid	Ester	Time min.			Found	Lit. (Ref. 2)
<u>hexanoic</u>	13.4489	35.9987	35	(0.83)	0.310	(1.00)	1.00
isovaleric	25.6217	10.5536		0.80	0.752	0.26	0.236
2-ethylhexanoic	45.3811	1.1088		0.86	0.979	0.022	0.0219
<u>heptanoic</u>	67.5817	240.3942	60	(0.86)	0.2458	(1.00)	1.00
2-ethyl-3-methyl- butanoic	280.0640	0.6275		0.83	0.9981	0.0020	0.00120
2-ethyl-3-methyl- butanoic	274.4355	9.0828	22	(0.86)	0.9723	(0.00120)	0.00120
triethylacetic	541.2249	0.4114	hr.	0.88	0.9993	0.000037	0.0000474

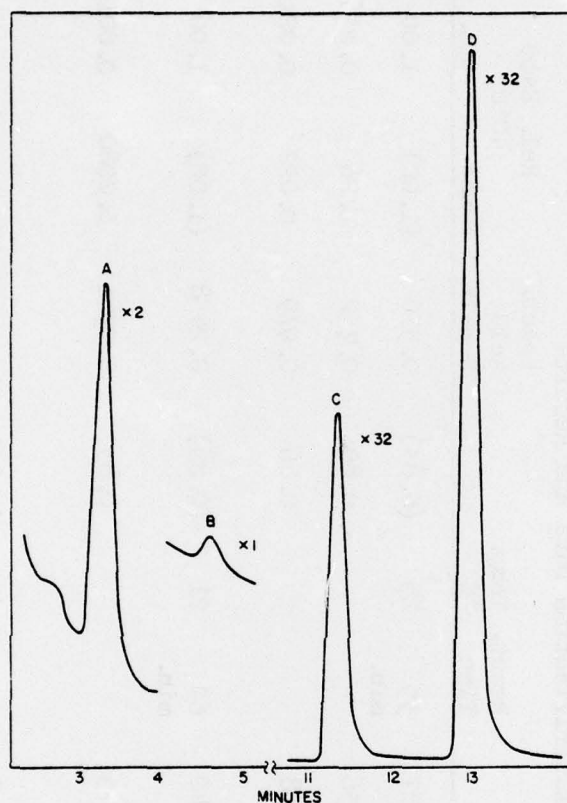


Fig. 1 — Chromatogram of the esterification results from Table 1, last set: (A) methyl 2-ethyl-3-methylbutanoate, (B) methyl triethylacetate, (C) 2-ethyl-3-methylbutanoic acid, and (D) triethylacetic acid.

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